Viscosities of Binary Mixtures of Carbon Tetrachloride with Methanol and Isopropyl Alcohol

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Measurements of viscosity as functions of composition of binary mixtures of carbon tetrachloride with methanol and isopropyl alcohol are reported. The results have been interpreted in terms of Eyring's relation for the viscosity of pure liquids and a self-consistent interaction energy, ω_{visc}, for each pair of unlike molecules.

IN SPITE of relative simplicity in the accurate experimental determinations of the viscosities of binary liquid mixtures, investigations in this direction are far from complete as no exhaustive theoretical treatment is available even for mixtures of simple molecules. Porter (*13*), Faust (*3*), Friend (*4*), and Nissan, Clark, and Nash (*12*) have noticed that a certain antiparallelism exists between the vapor pressure and viscosity. The deviations of the vapor pressures from Raoult's law are usually associated with deviations of the opposite sign from the equations for the viscosities of the ideal mixtures. Grunberg (*5*), and Reed and Taylor (*14*) have attempted to study the deviation from ideality of viscosities of binary liquid mixtures in terms of those of the pure liquids and the interaction between the pairs of unlike molecules. Studies by Katti and Chaudhri (*8*) on the variations in the viscosities as functions of composition of binary mixtures of benzyl acetate with dioxane, aniline, and *m*-cresol have revealed that a treatment of viscosities of mixtures based on Eyring's theory of viscosities of pure liquids—assuming a regular solution-type model for the activation free energy—represents rather well the dependence of mixture viscosities on composition. This article reports viscosities of binary mixtures of carbon tetrachloride with methanol and isopropyl alcohol. Boiling points (*9*) and surface tensions (*10*) of these binary mixtures have been investigated by Katti and Om Prakash. Excess free energy, heats of mixing, and entropies of one of the systems (methanol and carbon tetrachloride) have been fully studied by Scatchard and coworkers (*15*).

EXPERIMENTAL

Throughout the investigation, best available grades of Merck's methanol and isopropyl alcohol and B.D.H. (British Drug House) analar carbon tetrachloride have been used. Pure liquids from freshly opened bottles were subjected to further purification (*2*) whenever it was found necessary. The boiling points and densities of the samples of methanol, isopropyl alcohol, and carbon tetrachloride, finally selected for investigation (shown in Table I), agreed very well with the corresponding values quoted in the literature. Viscosities of the pure liquids and mixtures at different mole-fractions of methanol and isopropyl alcohol were determined at fixed temperature (40° C.). The measurements were carried out in an Ostwald viscometer which, for distilled water, gave a time period of flow of 1200 seconds. The temperature of the thermostat bath remained constant to within ± 0.008° C. as shown by a 1° C. range Beckmann thermometer reading up to

Table I. Comparison of the Physical Properties of the Liquids

Component	Densities at 40° C., Grams Per Ml. For specimen used	From literature	Boiling Points ° C. under a Pressure of 760 mm. of Hg, ° C. For specimen used	From literature	Viscosities at 40° C., Centipoise For specimen used	From literature
Methanol	0.7723	0.77232 (*7*)	64.60	64.65 (*6*)	0.4560	0.4560 (*6*)
Isopropyl alcohol	0.7690	0.7691 (*7*)	82.30	82.3 (*6*)	1.3300	1.33 (*1*)
Carbon tetrachloride	1.5550	1.55501 (*7*)	76.70	76.7 (*16*)	0.7390	0.7390 (*6*)

Table II. Viscosities in Centipoise of Methanol (Component 1) and Carbon Tetrachloride (Component 2) at 40° C.

$\omega_{vsic} = 685.5$ cal./mole

Mole Fraction of Methanol x	Molar Volume V	η_{ideal}	η_{obs}	η_{calcd}
0.000	98.9318	0.7390	0.7390	0.7390
0.105	92.6747	0.6847	0.7595	0.7593
0.193	87.5893	0.6430	0.7624	0.7633
0.303	81.4310	0.5961	0.7500	0.7522
0.350	78.6492	0.5792	0.7427	0.7441
0.510	69.2764	0.5299	0.6955	0.6978
0.680	59.8785	0.4870	0.6248	0.6189
0.720	57.6167	0.4795	0.6050	0.5986
0.790	53.6980	0.4680	0.5700	0.5618
0.910	46.4183	0.4602	0.5050	0.5037
1.000	41.4865	0.4560	0.4560	0.4560

Table III. Viscosities in Centipoise of Isopropyl Alcohol (Component 1) and Carbon Tetrachloride (Component 2) at 40° C.

$\omega_{vsic} = -466.6$ cal./mole

Mole Fraction of Isopropyl Alcohol χ	Molar Volume V	η_{ideal}	η_{obs}	η_{calcd}
0.000	98.9318	0.7390	0.7390	0.7390
0.115	96.7922	0.7864	0.7291	0.7286
0.220	94.6129	0.8350	0.7336	0.7340
0.325	92.2747	0.8882	0.7548	0.7535
0.421	90.1271	0.9404	0.7812	0.7833
0.500	88.4008	0.9860	0.8175	0.8175
0.602	86.2733	1.0473	0.8746	0.8751
0.685	84.6282	1.0990	0.9355	0.9348
0.745	83.3297	1.1399	0.9868	0.9884
0.879	80.3168	1.2396	1.1448	1.1450
1.000	78.1404	1.3300	1.3300	1.3300

0.001° C. Temperatures were measured on the International Scale with a calibrated copper-constantan thermocouple and a Pye-type precision vernier potentiometer. The densities were measured in a calibrated pycnometer of the type previously used by Mathot and Desmyter (*11*) and were reproducible to ± 0.0001 gram per ml. The viscosities reported here are accurate to within 0.5%. This margin has been estimated as the maximum limit from the corresponding possible uncertainties in the control of temperature and in the measurements on the times of flow, the compositions, and densities of mixtures. Auxiliary experiments dealing with a large number of observations on the viscosity at equimolar composition showed that the deviations of the individual observations, $(\Delta\eta/\eta) \times 100$, from the mean value η where much less than the 0.05% estimated limit. The results obtained are shown in Tables II and III.

RESULTS AND DISCUSSION

In columns 2 and 4 of Tables II and III are recorded the experimentally observed values of the molar volumes, V, and viscosities, η, against the mole fraction, χ, of one component shown in the corresponding row of column 1.

In column 5 are recorded the corresponding values of the viscosities of the mixtures calculated by using the relation (*8*)

$$\ln \eta_s V_s = \chi \ln \eta_1 V_1 + (1 - \chi) \ln \eta_2 V_2 + \chi(1 - \chi)\omega_{\text{visc}}/RT \quad (1)$$

where the symbols s, 1, and 2 stand for mixture and pure components 1 and 2, respectively; and ω_{visc} is the interaction energy for the activation of flow; R, the gas constant and T, the absolute temperature. A self-consistent value of ω_{visc} for each mixture was calculated by using Relation 1 from the observed values of η_s for an equimolar mixture. The corresponding values of ω_{visc} for each mixture are recorded at the head of Tables II and III.

The composition variations of the viscosities were then calculated by using the above values of ω_{visc} and Relation 1. These values are recorded in column 5 of Tables II and III. Column 3 shows the viscosities of the corresponding ideal mixtures as calculated from Relation 1 with ω_{visc} = zero.

A comparison of the corresponding viscosities for both the mixtures in columns 3 and 4 of Tables II and III shows the large deviations of these mixtures from ideality.

Columns 4 and 5 show that agreement between the experimentally observed values of viscosities and those calculated from Relation 1 for both the mixtures over the entire range of composition is well within the experimental error.

ACKNOWLEDGMENT

The authors are grateful to the Council of Scientific and Industrial Research for financial assistance.

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Received for review June 7, 1965. Accepted September 23, 1965.

Refractive Indices of Binary Hydrocarbon Mixtures

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Refractive indices, n_D, were determined for five binary hydrocarbon mixtures and correlated by means of a two-constant equation. When volume farctions were used instead of mole fractions, n_D values for four benzene–aliphatic hydrocarbon mixtures could be correlated by a one-constant equation.

IN THE STUDY of thermodynamic properties of mixtures, refractive indices were measured at 25° C. for five binary hydrocarbon mixtures: benzene-*n*-hexane, benzene-*n*-heptane, benzene-*n*-octane, benzene-*n*-decane, and benzene-cyclohexane. Measurements were made using a precision refractometer, and refractive indices were readily determined to 0.00001. The accuracy of reading is, however, of the order of 0.00003. A precision temperature controller was used to maintain the temperature at 25 ± 0.02° C. Spectro grade benzene and cyclohexane, (Matheson, Coleman, and Bell Co.), and research grade *n*-hexane and *n*-heptane, and pure grade *n*-octane and *n*-decane, (Phillips Petroleum Co.), were dried with silica gel and then used without further purifications. Experimental refractive index values of these pure compounds are compared with the literature values in Table I. Refractive indices of the five binary mixtures are listed in Table II. The uncertainty in making up mixtures, in terms of the liquid mole fraction, is estimated to be less than ± 0.0004.

The following equation has been used sucessfully in the literature for correlating thermodynamic properties of binary mixtures.

$$G = x_1G_1 + x_2G_2 + \frac{x_1x_2}{A + B(x_1 - x_2) + \cdots} \quad (1)$$